Equivalent Chemical Bonds Formed by s, p, and d Eigenfunctions*

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1. The work of Pauling on the linear combinations of eigenfunctions to form bond functions has been extended.

2. A theorem concerning the maximum strength in a given direction of a bond function orthogonal to existing bond functions has been derived. It is found that the strongest bond functions must lie at such angles to one another that the maximum of each coincides with a node of each of the others.

3. A general expression for equivalent Pauling bond functions formed from linear combinations of *s*, *p*, and *d* eigenfunctions has been derived.

4. By assuming the bond functions to have cylindrical symmetry, like the best possible bond functions, the equations can be readily solved. It is found that equivalent cylindrical bond functions will be orthogonal if the angles between every pair have no more than two values. The angles must be greater than 54°44′ and their sum must be greater than 180°; otherwise they are unrestricted. No more than six such bond functions may be formed. Solutions for six and less equivalent bond functions are given.

5. There are only four possible configurations for six equivalent cylindrical bond functions. Two of these are much weaker than the other two and so are improbable. The configurations for the stronger bond functions are in striking agreement with the only two structures, the octahedron and the trigonal prism, which are found experimentally.

6. A discussion of the factors influencing bond energies is made and examples of chemical compounds cited. It is predicted that the structure of P_4 is that of a tetrahedron with a P atom at each corner.

I. INTRODUCTION

IN THE theory of directed bonds of Pauling and Slater the bonds formed by a given atom tend to assume certain directions relative to one another; namely, those in which the single electron eigenfunctions of the atom have their maximum concentration, permitting maximum "overlapping" with the eigenfunctions of the other atoms with which bonds are formed. The prediction of bond angles is reduced by this theory to the determination of these directions; moreover, some information regarding the strength of a bond can be obtained from the consideration of the amount of concentration of the bond eigenfunction in the bond direction.

In the simple approximate treatment given by Pauling,[1] it is assumed that the bond eigenfunctions are formed by linear combination of a set of eigenfunctions

$$\Psi_{nlm}(r, \theta, \phi) = R_{nl}(r) P_l^{|m|}(\cos\theta) \{A \cos m\phi + B \sin m\phi\}$$

($P_l^m(\cos\theta)$ is Ferrer's associated Legendre polynomial)

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[1] Linus Pauling, J. Am. Chem. Soc. **53**, 1367 (1931).

which have approximately the same energy. The coefficients in the linear combinations are determined by a consideration of the θ, ϕ parts of the functions only, it being assumed that the r parts are similar (though not identical) in all of the functions. Neglecting the r part, the eigenfunctions with $l=0$, 1, and 2, $\cdots$ normalized to 4π, are:

$$
\begin{aligned}
s &= P_0^0(\cos\theta) && = 1\\
p_z &= (3)^{1/2}P_1^0(\cos\theta) && = (3)^{1/2}\cos\theta\\
p_x &= (3)^{1/2}P_1^1(\cos\theta)\cos\phi && = (3)^{1/2}\sin\theta\cos\phi\\
p_y &= (3)^{1/2}P_1^1(\cos\theta)\sin\phi && = (3)^{1/2}\sin\theta\sin\phi\\
d_z &= (5)^{1/2}P_2^0(\cos\theta) && = \tfrac{1}{2}(5)^{1/2}(3\cos^2\theta-1)\\
d_{x+z} &= [(15)^{1/2}/3]P_2^1(\cos\theta)\cos\phi && = (15)^{1/2}\sin\theta\cos\theta\cos\phi\\
d_{y+z} &= [(15)^{1/2}/3]P_2^1(\cos\theta)\sin\phi && = (15)^{1/2}\sin\theta\cos\theta\sin\phi\\
d_x &= [(15)^{1/2}/12]P_2^2(\cos\theta)\cos 2\phi && = \tfrac{1}{2}(15)^{1/2}\sin^2\theta\cos 2\phi\\
d_{x+y} &= [(15)^{1/2}/12]P_2^2(\cos\theta)\sin 2\phi && = \tfrac{1}{2}(15)^{1/2}\sin^2\theta\sin 2\phi
\end{aligned}
$$

The maximum values of these eigenfunctions are 1.000 for s, 1.732 for p_x, p_y, and p_z, 2.236 for d_z, and 1.936 for the other d eigenfunctions. For polar graphs of these see reference 1. (More bond functions of the same shape and strength as the d_z function can be formed by linear combinations of the other d functions.) These values are called the "strengths" of the bond functions, inasmuch as they indicate the amount of concentration of the functions in particular directions and hence give a rough measure of the bond-forming power of the functions. The meaning of the *strength* in terms of energy units has not been determined, but the resonance energy undoubtedly increases rapidly with the strength.

In certain cases, as in C ($1s^2 2s2p2p2p$), the s-p quantization may be broken and stronger bond functions can then be formed using linear combinations of s and p eigenfunctions. The strongest possible s-p bond functions have a strength of 2.000 and are directed to the four corners of a tetrahedron, in agreement with the tetrahedral carbon atom long known to organic chemists and accounting for many other bond angles of about 109°28′.[1]

For elements of the long periods, the d eigenfunctions probably play an important part in bond formation, since, for example, the $3d$ term value for elements of the first long period has probably not a greatly different energy from that of the $4s$ level. Just as in the case of s and p eigenfunctions the quantization may be broken and s-p-d, s-d, or p-d combinations may be formed.

In this paper a method for finding the best equivalent s-p-d bond functions will be developed. The equations prove to be too complex to be solved in the general case, but by making the reasonable assumption that the bond functions have cylindrical symmetry (the best possible bond functions do have cylindrical symmetry), solutions are obtained which cannot be far from the best.

II. The Maximum Strength of Bond Functions

It has been shown by Pauling (reference 1) that the strongest bond function $\Psi_j=\sum_{k=1}^{m}a_{jk}\psi_k(\theta,\phi)$ which can be formed in the direction θ_0, ϕ_0 has a

strength in that direction $\Psi_j(\theta_0,\phi_0) = \{\sum_{k=1}^{m}[\psi_k(\theta_0, \phi_0)]^2\}^{1/2}$. If it be required that this bond function be orthogonal to n pre-existing bond functions $\Psi_i(\theta, \phi) = \sum_{k=1}^{m} a_{ik}\psi_k(\theta, \phi)$, it can be shown (See appendix I) that the maximum strength is reduced to

$$\Psi_j(\theta_0, \phi_0) = \left\{ \sum_{k=1}^{m}[\psi_k(\theta_0, \phi_0)]^2 - \sum_{i=1}^{n}[\Psi_i(\theta_0, \phi_0)]^2 \right\}^{1/2}.$$

When the range of summation m comprises only completed subgroups, the first term is equal to m, and the formula becomes

$$\Psi_j(\theta_0, \phi_0) = \left\{ m - \sum_{i=1}^{n}[\Psi_i(\theta_0, \phi_0)]^2 \right\}^{1/2}.$$

If some of the eigenfunctions of the subgroups are excluded from bond formation, as is the case when they are occupied by an unshared pair of electrons, the formula still holds, providing these excluded eigenfunctions are treated as pre-existing bond functions.

This theorem gives us several important conclusions at once. *The strongest bond functions lie at such angles to one another that the maximum of each coincides with a node of each of the others.* In general, only three such bond functions are geometrically possible. For *s-p* bond functions, however, as we have seen, the nodal angle of 109°28′ allows the construction of four.

The best *s-p-d* bond function (reference 1) (with the maximum along the z axis) is

$$\Psi = \frac{1}{3}s + \frac{1}{(3)^{1/2}}p_z + \frac{(5)^{1/2}}{3}d_z.$$

It has a strength of $(9)^{1/2}$ and has nodes at 73°09′ and 133°37′. We may conclude that *s-p-d bonds tend to form at angles of 73°09′ and 133°37′. The closer the bond angles approach these values, the greater will be the resonance energy of the bond.* Only three of these bonds are geometrically possible and, as will be shown later, these angles may be modified considerably in the case of larger coordination numbers by orthogonality conditions.

In the same way it may be seen that the best *p* bond functions have a strength of $(3)^{1/2}$ and are formed at angles of 90°; the best *d* bond functions have a strength of $(5)^{1/2}$ and angles 54°44′ and 125°16′; the best *p-d* bond functions have a strength $(8)^{1/2}$ and angles 65°44′ and 144°12′; and the best *s-d* bond functions have a strength $(6)^{1/2}$ and angles 63°26′ and 116°34′.

III. Equivalent Bond Functions

Two bond functions may be defined as equivalent when they differ from one another by a rotation only. A method of finding equivalent bonds is to set up the most general *s-p-d* eigenfunction containing shape parameters and orientation parameters. Two eigenfunctions with the same values of the shape parameters will be equivalent.

Denoting the generalized eigenfunctions by capital letters, we have:

$$P = ap_z + bp_x + cp_y = \frac{(3)^{1/2}}{r}(ax + by + cz).$$

But by a rotation transformation P can be expressed as $a'z'/r$, with z' measured along an axis with direction cosines $a:b:c$. Hence a, b, and c are orientation and not shape parameters, and the most general shape of P is $P=p_z$. It may also be shown (See appendix II) that the most general D eigenfunction has the shape of a linear combination of d_z and d_x.

We can now express the most general *s-p-d* bond function as a linear combination of arbitrarily oriented S, P, and D eigenfunctions. The most general shape of the function, that is, the shape of the polar graph of strength against direction, will be determined by five parameters; three of them determine the relative amounts of s, p_z, d_z, and d_x which are in the bond (there are not four because of the normalization condition), and two the relative orientation of P to D. The orientation parameters may be determined by carrying out a rotation transformation on these eigenfunctions. This may be most conveniently done by rotating the axes as follows: Rotate through an angle ϕ_d' about the z axis, then through θ_d about the y axis, then through ϕ_d about the z axis. The behavior of our functions under these transformations is discussed in appendix III, in which the following expression for an *s-p-d* bond function of arbitrary shape and orientation is obtained:

$$\begin{aligned}
\Psi = {} & \sin\alpha \sin\beta\, s + \sin\alpha \cos\beta \{ [\cos\theta_p \cos\theta_d - \sin\theta_p \sin\theta_d \cos(\phi_p + \phi_d')]p_z \\
& + [\cos\theta_p \sin\theta_d \cos\phi_d + \sin\theta_p \cos\theta_d \cos(\phi_p + \phi_d') \cos\phi_d \\
& - \sin\theta_p \sin(\phi_p + \phi_d') \sin\phi_d]p_x + [\cos\theta_p \sin\theta_d \sin\phi_d \\
& + \sin\theta_p \cos\theta_d \cos(\phi_p + \phi_d') \sin\phi_d + \sin\theta_p \sin(\phi_p + \phi_d') \cos\phi_d]p_y\} \\
& + \cos\alpha \{ [(3/2)\cos\gamma \cos^2\theta_d - \tfrac{1}{2}\cos\gamma + \tfrac{1}{2}(3)^{1/2} \sin\gamma \sin^2\theta_d \cos 2\phi_d']d_z \\
& + [\tfrac{1}{2}(3)^{1/2} \cos\gamma \sin^2\theta_d \cos 2\phi_d + \sin\gamma \cos 2\phi_d \cos 2\phi_d' \\
& - \tfrac{1}{2}\sin\gamma \sin^2\theta_d \cos 2\phi_d \cos 2\phi_d' - \sin\gamma \cos\theta_d \sin 2\phi_d \sin 2\phi_d']d_x \\
& + \tfrac{1}{2}(3)^{1/2} \cos\gamma \sin^2\theta_d \sin 2\phi_d + \sin\gamma \sin 2\phi_d \cos 2\phi_d' \\
& - \tfrac{1}{2}\sin\gamma \sin^2\theta_d \sin 2\phi_d \cos 2\phi_d' + \sin\gamma \cos\theta_d \cos 2\phi_d \sin 2\phi_d']d_{x+y} \\
& + [\tfrac{1}{2}(3)^{1/2} \cos\gamma \sin 2\theta_d \cos\phi_d + \sin\gamma \sin\theta_d \sin\phi_d \sin 2\phi_d' \\
& - \tfrac{1}{2}\sin\gamma \sin 2\theta_d \cos\phi_d \cos 2\phi_d']d_{x+z} + [\tfrac{1}{2}(3)^{1/2} \cos\gamma \sin 2\theta_d \sin\phi_d \\
& - \sin\gamma \sin\theta_d \cos\phi_d \sin 2\phi_d' - \tfrac{1}{2}\sin\gamma \sin 2\theta_d \sin\phi_d \cos 2\phi_d']d_{y+z}.
\end{aligned}$$

α, β = shape parameters determining relative amounts of S, P, and D used; γ = shape parameter determining relative amounts of d_z and d_x used; θ_p, ϕ_p = shape parameters determining relative orientation of P to D; θ_d, ϕ_d = direction of z axis after rotation; ϕ_d' = rotation of bond function about new z axis.

The eigenfunction is normalized as written and the only restrictions on the values of the coefficients are the orthogonality conditions. For n bond functions these give $\frac{1}{2}n(n-1)$ equations containing 5 shape parameters and $3n-3$ arbitrary orientation parameters (three may be arbitrarily chosen without loss of generality). The equations are not necessarily independent. If the number of independent equations exceeds the number of unknowns, they are said to be over-determined, and there is no solution. If the numbers are equal, there will be one or more single points in the hyper space which satisfy the equation; while if the number of equations is less, there will be sets of continuous solutions. For certain values of some of the parameters the number of independent equations may be reduced.

From other considerations it seems probable that nine equivalent bond functions (36 equations, 29 unknowns) cannot be formed. The existence of solutions for eight bond functions, having 28 equations and 26 unknowns, is doubtful; but for seven or less bond functions there probably should be continuous solutions.

Unfortunately the orthogonality equations are extremely complicated, each equation containing 46 terms and involving 11 parameters. But by making certain reasonable approximations, we can reduce the equations to a readily soluble form. The best possible *s-p-d* bond function is symmetrical about the direction where it has its maximum value and has the following values of the shape parameters:

$$\theta_p = 0 \text{ (then } \phi_p \text{ may be arbitrary)}, \qquad \alpha = \cos^{-1}(5)^{1/2}/3,$$
$$\gamma = 0, \qquad \beta = \cos^{-1}\tfrac{1}{2}(3)^{1/2}.$$

An increase in γ will quickly reduce the possible bond strength by scattering the d eigenfunction, so any really strong bond function must have γ nearly equal to zero. We may therefore set $\gamma = 0$ with a feeling of considerable confidence that this arbitrary restriction has not eliminated any important bond eigenfunctions which are not rather closely approximated by one of those remaining. The same argument applies to θ_p except that the decrease in strength is not rapid. We shall assume that the p part of the bond function has its maximum in the same direction as the d part ($\theta_p = 0$).

These assumptions enormously simplify the orthogonality equations; the number of terms is reduced from 46 to 9 and the number of parameters from 11 to 6. Furthermore the direction of the maximum value of the bond functions is easy to find; it is θ, $\phi = \theta_d$, ϕ_d. These are the only *s-p-d* combinations with cylindrical symmetry, and will be referred to as *cylindrical bond functions*.

IV. Cylindrical Bond Functions

The above treatment gives us the following expression for the general cylindrical bond function

$$\Psi = \sin\alpha \sin\beta\, s + \sin\alpha \cos\beta[\cos\theta_d p_z + \sin\theta_d \cos\phi_d p_x + \sin\theta_d \sin\phi_d p_y]$$
$$+ \tfrac{1}{2}\cos\alpha[(3\cos^2\theta_d - 1)d_z + (3)^{1/2}\sin^2\theta_d \cos 2\phi_d d_x + (3)^{1/2}\sin^2\theta_d \sin 2\phi_d d_{x+y}$$
$$+ (3)^{1/2}\sin 2\theta_d \cos\phi_d d_{x+z} + (3)^{1/2}\sin 2\theta_d \sin\phi_d d_{y+z}].$$

If we place one bond function with its maximum along the z axis, all bond functions orthogonal to it must obey the equation:

$$\sin^2\alpha \sin^2\beta + \sin^2\alpha \cos^2\beta \cos\theta_d + \tfrac{1}{2}\cos^2\alpha(3\cos^2\theta_d - 1) = 0.$$

This is a quadratic in $\cos\theta_d$ and so has two solutions in terms of α and β. Hence the equivalent cylindrical bond functions orthogonal to a function of a given shape must have the loci of their maxima in two cones, which are determined by the shape parameters. Conversely, any two angles will determine the shape parameters.

$$\sin\alpha = \left(\frac{(1-\cos\theta)(1-\cos\theta') - \frac{2}{3}}{(1-\cos\theta)(1-\cos\theta')}\right)^{1/2}$$

$$\sin\beta = \left(\frac{\cos\theta\cos\theta' + \frac{1}{3}}{(1-\cos\theta)(1-\cos\theta') - \frac{2}{3}}\right)^{1/2}.$$

In order to have real solutions, the angles must be restricted as follows:

$$\theta, \theta' \geqq 54°44' \quad \theta + \theta' \geqq 180°.$$

Then all bond functions having their maxima at angles θ or θ' to the maximum of the given bond function will be orthogonal to it, providing the shape parameters are chosen correctly. This can easily be extended by symmetry to include all bond functions of the set, giving the general theorem: *The necessary and sufficient condition for a set of equivalent s-p-d cylindrical bond functions to be orthogonal is that there be no more than two different values for the angles between the direction of the maximum of any given bond function and the direction of the maxima of all the other bond functions.* The shape parameters must be chosen and the angles restricted as given above.

This theorem reduces our problem to the purely geometrical one of finding the ways that n vectors may be oriented such that the angles between all pairs obey the above restriction. It can be easily shown that no more than six vectors may be so placed: *No more than six equivalent cylindrical bond functions can be orthogonal to one another.*

For any values of the angles which satisfy the orthogonality conditions, the strength will be found to be

$$\text{Strength} = \frac{(\cos\theta\cos\theta' + \frac{1}{3})^{1/2} + (-3(\cos\theta + \cos\theta'))^{1/2} + (10/3)^{1/2}}{((1-\cos\theta)(1-\cos\theta'))^{1/2}}.$$

Six equivalent cylindrical bond functions

If we place one vector along the z axis, there may be as many as five in the θ cone, if they are evenly spaced; that is, $\Delta\phi = 72°$ or 144°. If we now make the angles between the vectors equal to θ or θ' by use of the distance formula of spherical trigonometry: $\cos\delta = \cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)$ where in this case $\delta = \theta$ or θ'; θ_1 and $\theta_2 = \theta$; and $\phi_1 - \phi_2 = 72°$ or 144°, we get two similar solutions. Placing four bonds in the θ cone and one in the θ' gives us another solution, the octahedral configuration discovered by Pauling.[1] There

is only one more solution; in which the vectors point to the corners of an equilateral triangular prism with square sides.

The first two solutions contain no p eigenfunctions. They are the strongest s-d bond functions that can be formed.

The six equivalent octahedral eigenfunctions[1] are:

$$\Psi_1 = \frac{1}{6^{1/2}}s + \frac{1}{2^{1/2}}p_z + \frac{1}{3^{1/2}}d_z,$$

$$\Psi_2 = \frac{1}{6^{1/2}}s - \frac{1}{2^{1/2}}p_z + \frac{1}{3^{1/2}}d_z,$$

$$\Psi_3 = \frac{1}{6^{1/2}}s + \frac{1}{2^{1/2}}p_x - \frac{1}{12^{1/2}}d_z + \tfrac{1}{2}d_x,$$

$$\Psi_4 = \frac{1}{6^{1/2}}s - \frac{1}{2^{1/2}}p_x - \frac{1}{12^{1/2}}d_z + \tfrac{1}{2}d_x,$$

$$\Psi_5 = \frac{1}{6^{1/2}}s + \frac{1}{2^{1/2}}p_y - \frac{1}{12^{1/2}}d_z - \tfrac{1}{2}d_x,$$

$$\Psi_6 = \frac{1}{6^{1/2}}s - \frac{1}{2^{1/2}}p_y - \frac{1}{12^{1/2}}d_z - \tfrac{1}{2}d_x,$$

with three pure d eigenfunctions orthogonal to them

$$\Psi_7 = d_{x+y};\ \Psi_8 = d_{x+z};\ \Psi_9 = d_{y+z}.$$

The trigonal prism eigenfunctions are:

$$\Psi_1 = \frac{51^{1/2}}{18}s + \frac{1}{6^{1/2}}p_z + \tfrac{1}{3}2^{1/2}p_x + \frac{1}{6(3)^{1/2}}d_z + \tfrac{1}{3}d_x + \frac{1}{3^{1/2}}d_{x+z}$$

$$\Psi_2 = \frac{51^{1/2}}{18}s + \frac{1}{6^{1/2}}p_z - \tfrac{1}{6}2^{1/2}p_x + \frac{1}{6^{1/2}}p_y + \frac{1}{6(3)^{1/2}}d_z - \frac{1}{6}d_x - \frac{1}{2(3)^{1/2}}d_{x+y} - \frac{1}{2(3)^{1/2}}d_{x+z} + \tfrac{1}{2}d_{y+z}$$

$$\Psi_3 = \frac{51^{1/2}}{18}s + \frac{1}{6^{1/2}}p_z - \tfrac{1}{6}2^{1/2}p_x - \frac{1}{6^{1/2}}p_y + \frac{1}{6(3)^{1/2}}d_z - \tfrac{1}{6}d_x + \frac{1}{2(3)^{1/2}}d_{x+y} - \frac{1}{2(3)^{1/2}}d_{x+z} - \tfrac{1}{2}d_{y+z}$$

$$\Psi_4 = \frac{51^{1/2}}{18}s - \frac{1}{6^{1/2}}p_z + \tfrac{1}{3}2^{1/2}p_x + \frac{1}{6(3)^{1/2}}d_z + \tfrac{1}{3}d_x - \frac{1}{(3)^{1/2}}d_{x+z}$$

$$\Psi_5 = \frac{51^{1/2}}{18}s - \frac{1}{6^{1/2}}p_z - \tfrac{1}{6}2^{1/2}p_x + \frac{1}{6^{1/2}}p_y + \frac{1}{6(3)^{1/2}}d_z - \tfrac{1}{6}d_x$$
$$- \frac{1}{2(3)^{1/2}}d_{x+y} + \frac{1}{2(3)^{1/2}}d_{x+z} - \tfrac{1}{2}d_{y+z}$$

$$\Psi_6 = \frac{51^{1/2}}{18}s - \frac{1}{6^{1/2}}p_z - \tfrac{1}{6}2^{1/2}p_x - \frac{1}{6^{1/2}}p_y + \frac{1}{6(3)^{1/2}}d_z - \tfrac{1}{6}d_x$$
$$+ \frac{1}{2(3)^{1/2}}d_{x+y} + \frac{1}{2(3)^{1/2}}d_{x+z} + \tfrac{1}{2}d_{y+z}$$

with the following eigenfunctions remaining.

$$\Psi_7 = \frac{1}{18^{1/2}}s - \frac{17^{1/2}}{18^{1/2}}d_z; \quad \Psi_8 = \frac{1}{3^{1/2}}p_x - \frac{2^{1/2}}{3^{1/2}}d_x; \quad \Psi_9 = \frac{1}{3^{1/2}}p_y + \frac{2^{1/2}}{3^{1/2}}d_{x+y}.$$

Five equivalent cylindrical bond functions

Solutions may of course be obtained by leaving out one bond function of our six-bond solutions. There is also a solution obtained by placing four bond

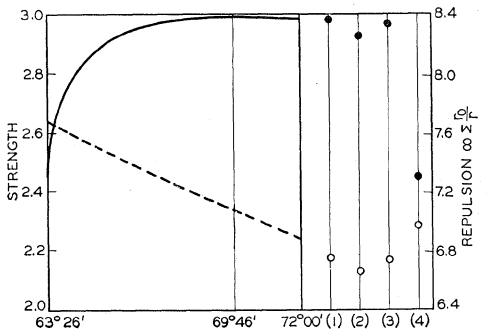

Fig. 1. Strengths of five equivalent cylindrical bonds for all possible configurations. The dotted curve represents a quantity proportional to the energy of possible electrostatic repulsion between the atoms surrounding the central atom. The configuration of maximum strength and minimum repulsion is favored. (1) $\theta = 81°\ 47'$; $\theta' = 135°\ 35'$, (2) $\theta = 90°$; $\theta' = 180°$ (3) $\theta = 120°$; $\theta' = 75°\ 31'$ (4) $\theta = 63°\ 26'$; $\theta' = 116°\ 34'$.

functions equally spaced in a cone 120° from the fifth bond function. These bond functions have a strength of 2.968, with $\theta' = 75°31'$. The conditions are also satisfied by the following relation between θ and θ'.

$$\cos\theta' = \tfrac{1}{2}(3 \pm (5)^{1/2})\cos\theta - \tfrac{1}{2}(1 \pm (5)^{1/2}).$$

In these solutions the five bonds are equally spaced in a cone. The strengths are shown as a function of the angle θ in Fig. 1, the maximum strength being 2.994. The energies of steric repulsion are qualitatively indicated by the dotted line.

Four equivalent cylindrical bond functions

In this case there are six sets of continuous solutions, which include all the previously given solutions for a greater number of bond functions.

$$\cos\theta' = \tfrac{1}{2}(3\cos^2\theta - 1) \tag{1}$$

$$\cos\theta' = \frac{4\cos^2\theta}{1+\cos\theta} - 1 \tag{2}$$

$$\cos\theta' = \cos^2\theta \pm (1-\cos\theta)(\cos^2\theta + (3/2)\cos\theta + \tfrac{1}{2})^{1/2} \tag{3}$$

$$\cos\theta' = \pm\, 2\cos\theta - 1 \tag{4}$$

$$\cos\theta' = \tfrac{1}{2}(3\cos\theta - 1 + (5)^{1/2}(\cos\theta - 1)) \tag{5}$$

$$\cos\theta' = \tfrac{1}{2}[1 - \cos\theta - (5 + 2\cos\theta - 3\cos^2\theta)^{1/2}] \tag{6}$$

The strengths of bond functions for these solutions are shown in Fig. 2. The strongest bond function is obtained from solution (a). It has angles of 136°06′ and 73°49′ and a strength of 2.9992. Single points on two of the curves represent bond functions which contain no s, that is, they represent p-d bond functions. These are at the largest angles of solutions (a) and (d). The strengths here are respectively 2.828 and 2.817, only slightly weaker than the best p-d bond function, which has a strength of 2.8284.

V. Discussion and Application of Results

The configuration assumed by an actual molecule is not, of course, determined solely by the resonance energy but, rather, by the position of minimum potential energy. If the bond is to a considerable extent ionic in character, the resonance energy may become unimportant. In any case forces between the atoms surrounding the central atom, if they are large, will be expected to deform the bond angles from the positions where the bond functions are a maximum. These forces[2] may result from interaction between the dipoles of the bonds (electrostatic forces), from interaction between dipole and bond by induction, or by steric hindrance when atoms or groups are close together. For equivalent bonds, these forces will always tend to make the bond angle larger. The bond energy will also be influenced by the term values of the eigenfunctions used in the bond function and by the term values of the nonbonding electrons. If we neglect the energy of the perturbation caused by bond formation, that set of bond functions will be favored which allows the maximum number of electrons to occupy eigenfunctions of low term values. The energy of eigenfunctions occupied by unshared electron pairs will be more important that the energy of a bond eigenfunction because two electrons are involved compared with one in the bond. Unshared pairs are apt to occupy the eigenfunctions of lowest energy, so that these eigenfunctions cannot be used in the construction of bond functions.

[2] H. A. Stuart, Phys. Rev. **38**, 1372 (1931).

Six equivalent bonds

The first two solutions in Table I have an advantage only in case the p levels lie considerably lower than the others, in which case unshared pairs might occupy them and exclude them from bond formation; or if the p levels

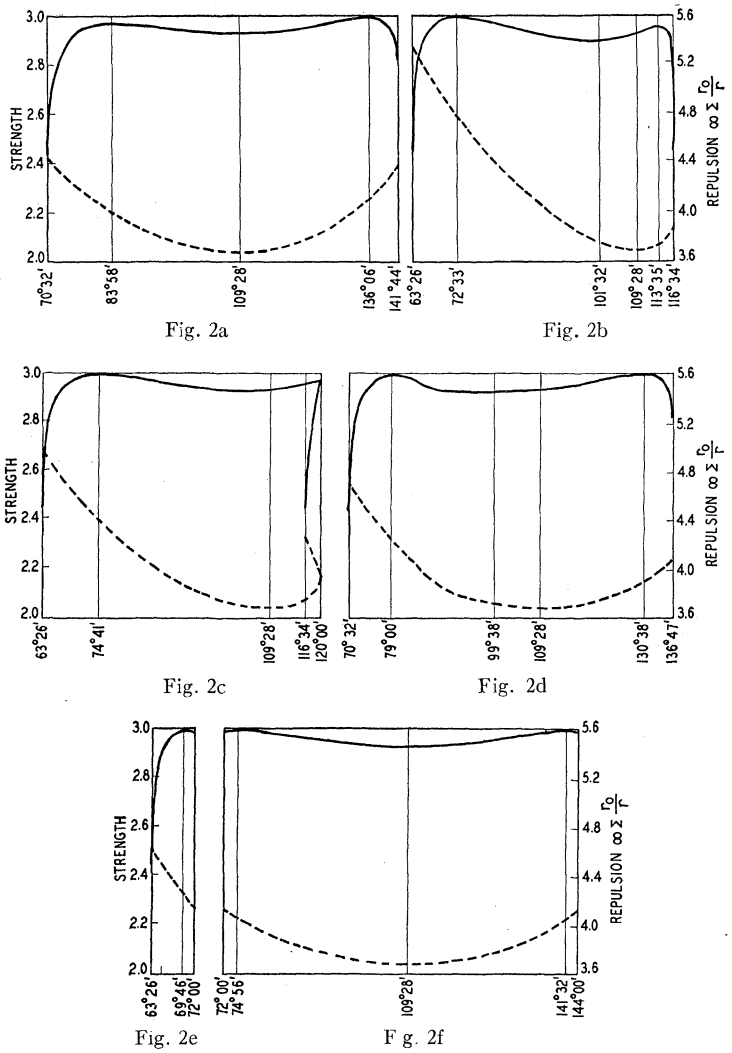

Fig. 2a Fig. 2b

Fig. 2c Fig. 2d

Fig. 2e F g. 2f

Fig. 2. Strengths and possible electrostatic repulsions of four equivalent cylindrical bonds.

lie considerably higher (with no unshared electron pairs present) so that it would be advantageous not to include them in the bond. There do not seem to be any atoms with large enough separations of energies to compensate for the much weaker bond functions of these solutions.

This leaves for consideration only two configurations, the octahedron and the trigonal prism. As a matter of fact, these are the only two structures

known experimentally, the former being found in the great majority of cases. The trigonal prism is found in molybdenite, MoS_2, and in tungstenite, WS_2. The quantitative experimental data for molybdenite[3] are in striking agreement with the theoretical structure. Each Mo atom is at the center of a trigonal prism whose six corners are occupied by sulfur atoms, the ratio of altitude to base of this regular triangular prism being 1.007 ± 0.039 compared to the theoretical ratio of 1.000.

TABLE I. *Sets of six equivalent cylindrical bond functions.*

	Angles between bonds θ	θ'	No. of angles θ	θ'	Bond strength	Remarks
(1)	63°26′	116°34′	10	5	2.449	Five bonds in cone. *s-d* bond fns.
(2)	116°34′	63°26′	10	5	2.449	Five bonds in cone. *s-d* bond fns.
(3)	90°00′	180°00′	12	3	2.924	Octahedral bonds
(4)	81°47′	135°35′	9	6	2.983	Trigonal prism bonds

The trigonal prism configuration has greater resonance energy per bond, but the octahedron has smaller repulsive forces between the surrounding atoms. The octahedron will be preferred for bonds which are appreciably ionic in character, or for large atoms surrounding the nuclear atom. Since it contains a smaller amount of *d*, it will also be favored where the *d* level lies highest, as in elements of the second period. Where the *d* level lies lowest, the trigonal prism will be favored, unless there are unshared electron pairs. One such pair can be accommodated in the second Ψ_7 eigenfunction given on page 898 which contains 17/18 *d*. But the second pair will have to be excited up to the Ψ_8 level. The fact that molybdenite is diamagnetic[4] indicates that in molybdenum this level is higher than Ψ_7 by an amount greater than the singlet-triplet separation. Hence, where the *d* level lies lowest, two or three unshared electron pairs strongly favor the octahedron, in which the pairs may all be placed in *d* levels.

Five equivalent bonds

The continuous solution gives a slight increase in resonance energy over the trigonal prism solution with one bond left out, but is considerably poorer sterically. The other new solution is poorer than the trigonal prism with one bond missing, both sterically and in bond strength. PCl_5, the structure of which is unknown, would be expected to have *s-p-d* bonds. It is difficult to estimate the magnitude of steric forces, but they are certainly much larger in PCl_5 than in molybdenite. Probably the octahedral configuration with one bond missing (square pyramid) of some sterically more favorable configuration involving non-cylindrical bonds is assumed by this molecule.

Four equivalent bonds

Neglecting a few exceptional regions, where other solutions give slightly better results, the solution shown in Fig. 2a is best both sterically and in bond

[3] Roscoe G. Dickinson and Linus Pauling, J. Am. Chem. Soc. **45**, 1466 (1923).
[4] E. B. Wilson, Jr., private communication.

strength. Bonds of this type will then lie at the configuration for maximum resonance energy, or will be deformed toward the tetrahedral configuration, the most favored sterically, along the curve given. If only one *d* eigenfunction is available, the best bonds are directed to the corners of a square, as shown by Pauling.[1]

As previously mentioned, *three equivalent bonds* of the maximum strength, 3.000, may be formed at angles of 73°09′ and 133°37′. For the configuration most favored sterically, three bonds in a plane at 120°, the strength is 2.881.

Two bonds of strength 3.000 at 133°37′ may be deformed to 180°, reducing the strength slightly to 2.96. This latter configuration will be expected when only one *d* eigenfunction is available. The functions are

$$\Psi_1 = (1/12^{1/2})s + (1/2^{1/2})p_z + (5^{1/2}/12^{1/2})d_z$$
$$\Psi_2 = (1/12^{1/2})s - (1/2^{1/2})p_z + (5^{1/2}/12^{1/2})d_z$$

with the unshared pair of electrons occupying

$$\Psi_3 = (5/6)^{1/2}\, s - (1/6)^{1/2} d_z$$

These are probably the bonds formed by silver in $Ag(CN)_2^-$($4d5s5p$ bonds), which is known to be linear.[5] Here the *s* and *d* levels have nearly the same energy, with the *p* level higher.

Other types of bonds

It may occur that the *s* level, when it lies lowest, will be occupied by an unshared pair of electrons, and *p-d* bonds will be formed. In order for *p-d* bonds to be orthogonal, the angles between them must satisfy the equation:

$$\sin^2 \alpha \cos \theta + \tfrac{1}{2} \cos^2 \alpha (3 \cos^2 \theta - 1) = 0.$$

As in the case of the *s-p-d* bond, there are two angles for a given shape of bond. But, since there is only one shape parameter, these angles are not independent. The specification of one angle determines the shape and strength of the bond and also the other possible angle.

Four p-d bonds. No more than four equivalent cylindrical *p-d* bonds may be formed. The two configurations given on page 899, although quite strong, are poor sterically. It is to be expected that SCl_4, which probably has this type of bond, will form a non-cylindrical bond with better steric properties.

Three p-d bonds. Three strongest bonds with a strength 2.828 can be formed at angles 65°44′ and 144°12′. In the molecule P_4 the phosphorus atoms may be bonded by *p* bonds or by *p-d* bonds. In the former case the bond angle would tend to be 90° and the most probable configuration would place the four *P* atoms at the corners of a square, connected by alternate single and double bonds. The single bond functions have a strength of 1.732, while the double bonds have much less than twice the energy of a single bond. Much stronger *p-d* bond functions can be formed if the *P* atoms are placed at the corners of a regular tetrahedron, with bond angles of 60°.

[5] J. L. Hoard, private communication

Bonds may be hindered from their tendency to form in the direction of the maximum of the bond function by steric or geometric factors, with an accompanying decrease in resonance energy. When this occurs, the bond function will rearrange itself so as to give a maximum strength in the new direction. The maxima of the rearranged bond functions will not lie in the directions of the bonds, but will generally assume positions between the bond directions and the directions of the undisturbed maxima. In this case, where the bonds tend to form at 65°44′ but are required by geometry to be at 60°, the maxima of the bond functions will be in directions 64°02′ apart, and their strength in the bond directions is 2.819. The bond functions are then

$$\Psi_1 = 0.4520p_z + 0.3500p_x + 0.3593d_z + 0.2663d_x + 0.6880d_{x+z}$$

$$\Psi_2 = 0.4520p_z - 0.1750p_x + 0.3031p_y + 0.3593d_z - 0.1332d_x - 0.2306d_{x+y} - 0.3440d_{x+z} + 0.5958d_{y+z}$$

$$\Psi_3 = 0.4520p_z - 0.1750p_x - 0.3031p_y + 0.3593d_z - 0.1332d_x + 0.2306d_{x+y} - 0.3440d_{x+z} - 0.5958d_{y+z}.$$

Where the bond directions are (35°16′, 0°), (35°16′, 120°), and (35°16′, 240°). The bonds are composed 32.67 percent of the p eigenfunctions. Bond functions with their maxima at 60° have a strength of only 2.773.

Two p-d bonds. Two bond functions may be formed at 180° with a strength of 2.806 as compared with the strongest bond functions at 144°12′ with a strength 2.828.

I wish to express my appreciation of the assistance of Professor Linus Pauling, at whose suggestion this problem was undertaken. I am also indebted to Dr. Boris Podolsky, now of Kharkov, for some of the rotation transformation formulas.

Appendix I

Problem

To construct the normalized bond function $\Psi_j = \sum_{k=1}^{m} a_{jk}\psi_k$ *with maximum value in the direction* θ_0, ϕ_0 *and orthogonal to n given orthogonal, normalized bond functions of the same type,*

$$\Psi_i = \sum_{k=1}^{m} a_{ik}\psi_k \qquad (i = 1, 2, 3, \cdots, n)(j \neq i). \tag{1}$$

The orthogonality and normalization conditions require

$$\sum_{k=1}^{m} a_{ik}a_{lk} = \delta_{il} \quad (= 0 \text{ where } i \neq l;\ = 1 \text{ where } i = l). \tag{2}$$

Let

$$\Lambda = \sum_{k=1}^{m} a_{jk}\psi_k - \frac{\lambda}{2}\left[\sum_{k=1}^{m} a_{jk}^2 - 1\right] - \sum_{i=1}^{n} \sum_{k=1}^{m} \mu_i a_{ik}a_{jk} = \Psi_j \tag{3}$$

Ψ_j will be a maximum when

$$\frac{\partial\Lambda(\theta_0, \phi_0)}{\partial a_{jk}} = 0 = \psi_k(\theta_0, \phi_0) - \lambda a_{jk} - \sum_{i=1}^{n}\mu_i a_{ik} \qquad k = (1, 2, \cdots, m). \quad (4)$$

Hence

$$a_{jk} = \frac{\psi_k(\theta_0, \phi_0) - \sum_{i=1}^{n}\mu_i a_{ik}}{\lambda}. \quad (5)$$

Multiplying this by a_{lk} $(l \neq j)$ and summing over k it is found that

$$\mu_l = \sum_{k=1}^{m} a_{lk}\psi_k = \Psi_l. \quad (6)$$

By squaring (5) and summing over k we get

$$\lambda = \left[\sum_{k=1}^{m}\psi_k^2 - \sum_{i=1}^{n}\Psi_i^2\right]^{1/2}. \quad (7)$$

Hence

$$a_{jk} = \frac{\psi_k - \sum_{i=1}^{n} a_{ik}\Psi_i}{\left[\sum_{k=1}^{m}\psi_k^2 - \sum_{i=1}^{n}\Psi_i^2\right]^{1/2}} \quad (8)$$

$$\Psi_j = \left[\sum_{k=1}^{m}\psi_k^2 - \sum_{i=1}^{n}\Psi_i^2\right]^{1/2}. \quad (9)$$

Corollary

When the m original eigenfunctions comprise only completed subgroups,

$$\sum_{k=1}^{m}\psi_k^2 = m \text{ and } \Psi_j = \left[m - \sum_{i=1}^{n}\Psi_i^2\right]^{1/2}.$$

Appendix II

Proof that the most general d eigenfunction (arbitrarily oriented) is a linear combination of d_z and d_x. The most general d eigenfunction is

$$\mathcal{D} = Ad_x + Bd_{x+y} + Cd_{x+z} + Dd_{y+z} + Ed_z$$

which in Cartesian coordinates is

$$\mathcal{D} = 1/r^2(a'x^2 + b'y^2 + c'z^2 + d'xy + e'xz + f'yz)$$

that is, the general quadratic. A rotation transformation will change the general quadratic to one containing squares only.

$$\mathcal{D} = 1/r^2(ax^2 + by^2 + cz^2).$$

The coefficients are restricted by the fact that D, to be an eigenfunction, must satisfy Laplace's equation; and also must be normalized, so that

$$a + b + c = 0$$

$$\int_\tau \mathcal{D}^2 d\tau = 4\pi.$$

The normalization equation when evaluated gives the relation

$$3(a^2 + b^2 + c^2) + 2(ab + ac + bc) = 15.$$

From the two relations we get

$$\mathcal{D} = ax^2 - \tfrac{1}{2}(a \pm (15 - 3a^2)^{1/2})y^2 - \tfrac{1}{2}(a \mp (15 - 3a^2)^{1/2})z^2.$$

But this may be obtained from

$$\mathcal{D} = a' d_x - (1 - a'^2)^{1/2} d_z$$

by setting

$$a = \tfrac{1}{2}(15)^{1/2} a' - \tfrac{1}{2}(5)^{1/2}(1 - a'^2)^{1/2}$$

Appendix III

Problem

To determine the behavior of S, P, and D under the general rotation transformation. If the coordinate axes are rotated for an angle ϕ_d' about the z axis, then an angle θ_d about the y axis, then again ϕ_d about the z axis, the coordinates of the point P, θ' and ϕ' appear as shown in Fig. 3, where all lines drawn are arcs of great circles.

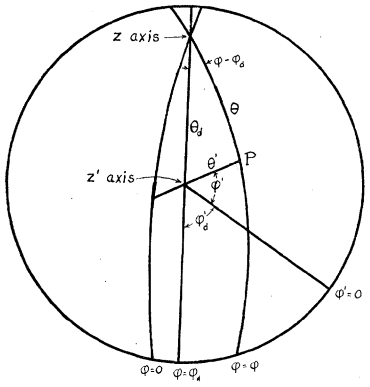

Fig. 3. Rotation of axes on the unit sphere.

By spherical trigonometry we have

$$\cos\theta' = \cos\theta_d \cos\theta + \sin\theta_d \sin\theta \cos(\phi - \phi_d)$$

$$\sin(\phi' + \phi_d') = \frac{\sin\theta \sin(\phi - \phi_d)}{\sin\theta'}$$

$$\cos(\phi' + \phi_d') = \frac{\cos\theta_d \sin\theta \cos(\phi - \phi_d) - \sin\theta_d \cos\theta}{\sin\theta'}.$$

We may easily solve these to get $\sin\phi'$, $\sin 2\phi'$, $\cos\phi'$, $\cos 2\phi'$ in terms of $\theta, \phi, \theta_d, \phi_d, \phi_d'$.

We also wish to evaluate

$$P_l^{|m|}(\cos\theta') = P_l^{|m|}[\cos\theta_d\cos\theta + \sin\theta_d\sin\theta\cos(\phi-\phi_d)].$$

This may be done by use of Gegenbauer C functions.*

$$P_l^{|m|}(\cos\theta') = \frac{(2m)!}{2^m m!}\sin^m\theta' C_{l-m}^{m+1/2}(\cos\theta').$$

But:

$$C_{l-m}^{m+1/2}(\cos\theta_d\cos\theta + \sin\theta_d\sin\theta\cos(\phi-\phi_d)) = \frac{\Gamma(2m)}{[\Gamma(m+\frac{1}{2})]^2}\times$$

$$\sum_{\lambda=0}^{l-m}\Big\{\frac{(-1)^\lambda 2^{2\lambda}\Gamma(l-m-\lambda+1)}{\Gamma(l+m+\lambda+1)}[\Gamma(m+\lambda+\tfrac{1}{2})]^2\times$$

$$(2m+2\lambda)\sin^\lambda\theta_d\sin^\lambda\theta C_{l-m-\lambda}^{m+\lambda+1/2}(\cos\theta_d)C_{l-m-\lambda}^{m+\lambda+1/2}(\cos\theta)C_\lambda^m(-\cos(\phi-\phi_d))\Big\}.$$

Making the following simplifications since l, m, and λ are integers

$$\Gamma(n) = (n-1)!$$

$$\Gamma(n+\tfrac{1}{2}) = \frac{(2n)!}{2^{2n}n!}(\pi)^{1/2}$$

where n is an integer

$$C_{l-m-\lambda}^{m+\lambda+1/2}(\cos x) = \frac{2^{m+\lambda}(m+\lambda)!}{(2m+2\lambda)!\sin^{m+\lambda}x}$$

$$C_\lambda^m(-x) = (-)^\lambda C_\lambda^m(x)$$

we obtain

$$P_l^{|m|}(\cos\theta') = \frac{m!2^m\sin^m\theta'}{\sin^m\theta_d\sin^m\theta}\sum_{\lambda=0}^{l-m}\frac{(l-m-\lambda)!(m+\lambda)}{(l+m+\lambda)!m}$$
$$P_l^{|m|+\lambda}(\cos\theta_d)P_l^{|m|+\lambda}(\cos\theta)C_\lambda^{|m|}(\cos(\phi-\phi_d).$$

Using these formulas we get for our general expressions of eigenfunctions rotated through arbitrary angles

$$s = P_0^0(\cos\theta') = 1$$

$$p_z = 3^{1/2}P_1^0(\cos\theta') = 3^{1/2}(\cos\theta_p\cos\theta + \sin\theta_p\sin\theta\cos(\phi-\phi_p))$$

$$d_z = 5^{1/2}P_2^0(\cos\theta') = \tfrac{1}{4}(5)^{1/2}\{(3\cos^2\theta_d - 1)(3\cos^2\theta - 1)$$

* See Whittaker and Watson, "Modern Analysis", Chap. XV for most of the formulas involving the Gegenbauer function.

$$+ 3 \sin 2\theta_d \sin 2\theta \cos(\phi - \phi_d) + 3 \sin^2\theta_d \sin^2\theta \cos 2(\phi - \phi_d)\}$$

$$d_x = \frac{1}{12}(15)^{1/2}P_2^2(\cos\theta')\cos 2\phi' = \tfrac{1}{2}(15)^{1/2}\{\sin^2\theta \cos 2(\phi - \phi_d)\cos 2\phi_d'$$

$$+ \tfrac{1}{2}(3\cos^2\theta - 1)\sin^2\theta_d \cos 2\phi_d' - \tfrac{1}{2}\sin^2\theta \cos 2(\phi - \phi_d)\sin^2\phi_d \cos 2\phi_d'$$

$$+ \sin^2\theta \sin 2(\phi - \phi_d)\cos\theta_d \sin 2\phi_d' - \sin 2\theta \sin(\phi - \phi_d)\sin\theta_d \sin 2\phi_d'$$

$$- \tfrac{1}{2}\sin 2\theta \cos(\phi - \phi_d)\sin 2\theta_d \cos 2\phi_d'\}.$$

By carrying the transformed p_z through a second rotation ϕ_d', θ_d, ϕ_d and expressing all angles θ and ϕ in terms of the original s, p, and d eigenfunctions we arrive at the expression given in the text for the most general eigenfunction.